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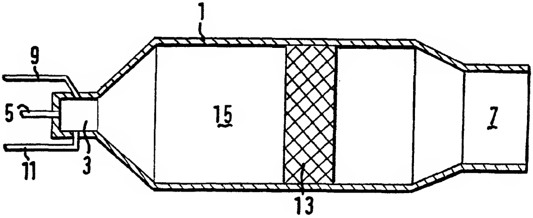
(54) **Claus reaction furnace**

(57) Claus reaction furnace comprising a housing (1), a burner (3) with gas inlets (5 and 9), a gas outlet (7), and a rigid permeable catalyst structure (13) arranged between the burner (3) and the gas outlet (7), which rigid permeable catalyst structure (13) includes a support and a catalytically active substance comprising at least 0.80 kg of alumina/kg and being provided with pores having a specific surface area between 0.5 and 100 m²/g.



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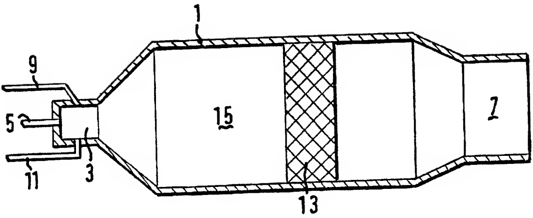

CLAUS REACTION FURNACE

The present invention relates to a Claus reaction furnace comprising a housing, a burner with gas inlets, and a gas outlet.

The gas outlet is normally in fluid communication with a waste heat boiler, condenser, and the first of a series of one or more interconnected catalytic reactors and other equipment.

During normal operation a feed gas, referred to as acidic feed gas, containing hydrogen sulphide, carbon dioxide and varying amounts of other components, including water, methane, ethane, other hydrocarbons and nitrogen, and air are supplied to the gas inlets of the Claus reaction furnace. The Claus reaction furnace is operated in such a way that part of the hydrogen sulphide is oxidised to sulphur dioxide which reacts with the remaining hydrogen sulphide to form elemental sulphur.

To complete the reaction the gas mixture from the Claus reaction furnace is cooled, sulphur is condensed and removed therefrom, and the remaining gas mixture is passed to the first catalytic reactor in which elemental sulphur is produced. From the first catalytic reactor a gas mixture including hydrogen sulphide, sulphur dioxide and elemental sulphur is passed via a condenser, where elemental sulphur is removed from the gas stream, to the second catalytic reactor. From the second catalytic reactor a gas mixture including hydrogen sulphide, sulphur dioxide and elemental sulphur is passed via a condenser, where elemental sulphur is removed from the gas stream, to the third catalytic reactor. In a last condenser elemental sulphur is removed from the gas mixture leaving the third catalytic reactor.

The above described Claus sulphur recovery unit contains three catalytic reactors, Claus sulphur recovery units can have between two to four catalytic reactors.

During normal operation of the Claus reaction furnace, varying amounts of organic sulphur compounds such as carbon disulphide and carbonyl sulphide are formed in addition to sulphur dioxide and sulphur. It has been postulated that carbon disulphide is formed by a reaction of hydrogen sulphide or sulphur with hydrocarbon impurities in regions of the furnace where unburned hydrocarbon exists. Carbonyl sulphide is probably formed by reaction of sulphur and carbon monoxide obtained from the reduction of carbon dioxide. Some of the organic sulphur compounds initially formed will decompose as the gas mixture passes through the reaction furnace and the associated equipment.

However, in some situations, in particular when the acidic feed gas has a relatively low hydrogen sulphide content, or a relatively high hydrocarbon content, or where the reaction furnace provides a relatively low gas residence time, the gas mixture leaving the Claus reaction furnace can contain relatively large amounts of organic sulphur compounds. It is not uncommon that 10% by weight or more of the sulphur in the gas mixture leaving the Claus reaction furnace of a susceptible Claus sulphur recovery unit is in the form of carbon disulphide and carbonyl sulphide.

If not converted to sulphur, these compounds will find their way to the tail gas, thereby either severely burdening any tail gas treating unit downstream of the sulphur recovery unit, or releasing unacceptable amounts of polluting sulphur-containing effluent to the atmosphere.

To reduce the amounts of carbon disulphide and carbonyl sulphide to required levels, the first catalytic reactor can be operated at a relatively high temperature, often as high as 380 to 400 °C at the outlet. This practice is very effective, but causes a loss of efficiency in the Claus reaction, in which hydrogen sulphide and sulphur dioxide react to form sulphur and water, since the equilibrium point for this reaction is favoured by low temperatures. In addition, catalysts used in the catalytic reactors suffer a loss of surface area when kept at high temperatures, especially in the presence of water vapour. For this reason, operators of

Claus sulphur recovery units normally try to limit the increase in temperature in the catalytic reactors, consistent with satisfactory conversion of carbon disulphide and carbonyl sulphide.

Much research effort has been expended over the years to improve the conversion of carbon disulphide and carbonyl sulphide, and many improved catalysts for this purpose have been developed. However, a further increase in temperature was avoided, because of the stated effects on the Claus reaction equilibrium, and catalyst stability.

It is an object of the present invention to provide a Claus reaction furnace which produces during normal operation a gas mixture which has a reduced amount of organic sulphur compounds.

To this end the Claus reaction furnace according to the invention comprises a housing, a burner with gas inlets, a gas outlet, and a rigid permeable catalyst structure arranged between the burner and the gas outlet, which rigid permeable catalyst structure includes a support and a catalytically active substance comprising at least 0.80 kg of alumina/kg and being provided with pores having a specific surface area between 0.5 and 100 m^2/g.

The invention will now be described by way of example in more detail with reference to the accompanying drawing showing schematically a cross-section of the Claus reaction furnace according to the invention.

The Claus reaction furnace comprises a housing 1, a burner 3 with gas inlets in the form of feed inlet 5 and air inlet 9, and a gas outlet 7.

The burner 3 is further provided with a fuel supply conduit 11.

In the housing 1 is arranged rigid permeable catalyst structure 13 located between the burner 3 and the gas outlet 7.

The rigid permeable catalyst structure 13 includes a support and a catalytically active substance comprising at least 0.80 kg of alumina/kg and being provided with pores having a specific surface area between 0.5 and 100 m^2/g.

The support of the rigid permeable catalyst structure comprises a refractory material having a working temperature of at least 1100 °C which supports the catalytically active substance.

During normal operation an acidic feed gas including hydrogen sulphide is supplied to the gas inlet 5 and oxidant is supplied to air inlet 9. Only during start-up, fuel is additionally supplied to the fuel supply conduit 11.

The Claus reaction furnace is operated in such a way that part of the hydrogen sulphide is oxidised to sulphur dioxide which reacts with the remaining hydrogen sulphide to form elemental sulphur.

The gas mixture passes through the longitudinal passages of the rigid permeable catalyst structure 13 where the organic sulphur compounds are converted into hydrogen sulphide. By arranging the rigid permeable catalyst structure in the housing the hot gas mixture is contacted with the catalytically active rigid permeable catalyst structure, which facilitates the conversion of organic sulphur compounds.

For an acidic feed gas containing about 0.50 mol hydrogen sulphide/mol, 0.42 mol carbon dioxide/mol, 0.04 mol methane/mol and 0.04 mol water, the gas mixture leaving the Claus reaction furnace comprises 0.02 mol hydrogen/mol, 0.48 mol nitrogen/mol, 0.02 mol carbon monoxide/mol, 0.14 mol carbon dioxide/mol, 0.03 mol hydrogen sulphide/mol, 0.05 mol sulphur dioxide/mol, 0.01 mol carbonyl sulphide/mol, 0.01 mol carbon disulphide and 0.04 mol sulphur (S_2)/mol, the balance being water. The average molecular weight is about 32.

In the Claus reaction furnace, the space velocity of the gas is between 360 and 7200 l gas/hour/l space, wherein the gas volume is given at 0 °C and at atmospheric pressure, and the temperature in the Claus reaction furnace is about 1000 °C.

If required the inner wall of the housing 1 can be lined with suitable refractory material.

In a suitable embodiment the catalytically active substance of the rigid permeable catalyst structure 13 includes at least 0.90 kg alumina/kg.

The support of the rigid permeable catalyst structure comprises a honeycomb of cordierite or mullite, the cell width is between 3 and 5 mm, and wherein the thickness of the walls between adjacent cells is between 0.1 and 5 mm. The honeycomb is so arranged that the gas passes through the cells.

In an alternative embodiment, the support of the rigid permeable catalyst structure is provided with longitudinal passages, extending in the direction of the gas flow, having a cross-sectional area between 0.2 and 78 mm^2. The support can comprise a layer of alumina-containing bricks.

The rigid permeable catalyst structure may entirely consist of the catalytically active substance.

In a further embodiment of the invention the rigid permeable catalyst structure comprises a layer of particles arranged between vertical screens.

Alternatively, the rigid permeable catalyst structure comprises fibres having a thickness between 0.1 and 5 mm.

The thickness of the rigid permeable catalyst structure is between 0.3 and 2 m. During normal operation the pressure drop over the rigid permeable catalyst structure should be less than about 3.5 kPa.

The rigid permeable structure can be placed anywhere in the furnace, but is suitably placed near the outlet of the reaction furnace, where the temperature is expected to be lower. The life of the catalyst will likely be longer at the lower temperature.

The following experiments were carried out to simulate the conversion of organic sulphur compounds using a permeable catalyst structure arranged in a Claus reaction furnace. The gas fed to the experimental unit contained no elemental sulphur, but contained increased amounts of hydrogen sulphide and sulphur dioxide, and a reduced amount of water, so that after reaction of these components, their concentrations closely simulated the gas composition

cited previously. The feed gas entered a quartz reactor having an inside diameter of 1 cm, which contained the catalyst sample heated to 1000 °C. Elemental sulphur and water were removed from the gas leaving the reactor, before the composition of the gas leaving the reactor was analysed using gas chromatography.

Experiment 1, not according to the invention. In this experiment the reactor was empty. The composition of the gas as supplied to the reactor was 0.0205 mol H_2/mol, 0.4857 mol N_2/mol, 0.0203 mol CO/mol, 0.1412 mol CO_2/mol, 0.0103 mol COS/mol, 0.0872 mol H_2S/mol, 0.0103 mol CS_2/mol, 0.0794 mol SO_2/mol and the balance being water. The molar flow rate of the gas was 0.84 mol/hour and the linear velocity was 0.31 m/s. The composition of the gas leaving the reactor was 0.4857 mol N_2/mol of feed, 0.1455 mol CO_2/mol of feed, 0.0074 mol COS/mol of feed, 0.0124 mol H_2S/mol of feed, 0.00887 mol CS_2/mol of feed, 0.0467 mol SO_2/mol of feed. The COS conversion was 29% and the CS_2 conversion 13.8%.

Experiment 2, according to the invention. In this experiment the reactor was provided with a rigid permeable catalyst structure in the form of 0.79 g of refractory particles having diameters in the range of from 1.2 to 1.7 mm, a surface area of 0.92 m^2/g. The composition of the particles was 0.94 kg Al_2O_3/kg, 0.002 kg SiO_2/kg, 0.053 kg CaO/kg, 0.002 kg Fe_2O_3/kg, 0.001 kg MgO/kg and the balance being alkali oxides. The composition of the gas as supplied to the reactor was 0.0197 mol H_2/mol, 0.4651 mol N_2/mol, 0.0195 mol CO/mol, 0.1310 mol CO_2/mol, 0.0113 mol COS/mol, 0.1055 mol H_2S/mol, 0.0126 mol CS_2/mol, 0.0903 mol SO_2/mol and the balance being water. The molar flow rate of the gas was 0.84 mol/hour, the linear velocity in the reactor was 0.31 m/s, and the space velocity in the reactor was 28822 l gas/hour/l space, wherein the gas volume is given at 0 °C and at atmospheric pressure. The composition of the gas leaving the reactor was 0.4651 mol N_2/mol of feed, 0.1484 mol CO_2/mol of feed, 0.0063 mol COS/mol of feed, 0.0500 mol H_2S/mol of feed, 0.0061 mol CS_2/mol of feed, 0.0570 mol SO_2/mol of feed. The COS conversion was 44% and the CS_2 conversion 99.5%.

Experiment 3, according to the invention. In this experiment the reactor was provided with a rigid permeable catalyst structure in the form of a one-cell specimen cut from a honeycomb coated with a catalytically active substance containing 0.9 kg Al_2O_3/kg. The length of the specimen was 5 cm, its mass was 1.71 g, the width of the square longitudinal hole was 4 mm and the thickness of the wall surrounding the hole was 1 mm. The surface area of the catalytically active substance was between 10-15 m^2/g. The composition of the gas as supplied to the reactor was 0.0205 mol H_2/mol, 0.4857 mol N_2/mol, 0.0203 mol CO/mol, 0.1412 mol CO_2/mol, 0.0103 mol COS/mol, 0.0872 mol H_2S/mol, 0.0103 mol CS_2/mol, 0.0794 mol SO_2/mol and the balance being water. The molar flow rate of the gas was 0.84 mol/hour, the linear velocity in the reactor was 0.31 m/s, and the space velocity in the reactor was 4814 l gas/hour/l space wherein the gas volume is given at 0 °C and at atmospheric pressure. The composition of the gas leaving the reactor was 0.4857 mol N_2/mol of feed, 0.1580 mol CO_2/mol of feed, 0.0036 mol COS/mol of feed, 0.0260 mol H_2S/mol of feed, 0.00018 mol CS_2/mol of feed, 0.0344 mol SO_2/mol of feed. The COS conversion was 65% and the CS_2 conversion 98.3%.

In conclusion, catalytically active substance comprising at least 0.80 kg of alumina/kg and being provided with pores having a specific surface area between 0.5 and 100 m^2/g were found to have very high activity for carbon disulphide conversion even though surface areas were much lower than those of normal first converter catalyst. By operating these catalysts at or close to the temperature of the reaction furnace, little or no deterioration of the Claus equilibrium will take place. The first catalytic stage, containing conventional Claus catalyst, can now be operated at lower temperatures, improving the yield of sulphur.

CLAIMS

1. Claus reaction furnace comprising a housing, a burner with gas inlets, a gas outlet, and a rigid permeable catalyst structure arranged between the burner and the gas outlet, which rigid permeable catalyst structure includes a support and a catalytically active substance comprising at least 0.80 kg of alumina/kg and being provided with pores having a specific surface area between 0.5 and 100 m^2/g.

2. Claus reaction furnace as claimed in claim 1, wherein the support comprises a refractory material having a working temperature of at least 1100 °C.

3. Claus reaction furnace as claimed in claim 1 or 2, wherein the catalytically active substance includes at least 0.90 kg alumina/kg.

4. Claus reaction furnace as claimed in any one of the claims 1-3, wherein the thickness of the rigid permeable catalyst structure is between 0.3 and 2 m.

5. Claus reaction furnace as claimed in any one of the claims 1-4, wherein the support of the rigid permeable catalyst structure comprises a honeycomb of cordierite or mullite arranged perpendicular to the fluid flow.

6. Claus reaction furnace as claimed in claim 5, wherein the cell width of the honeycomb is between 3 and 5 mm, and wherein the thickness of the walls between adjacent cells is between 0.1 and 5 mm.

7. Claus reaction furnace as claimed in any one of the claims 1-4, wherein the support is provided with longitudinal passages having a cross-sectional area between 0.2 and 78 mm^2.

8. Claus reaction furnace as claimed in claim 7, wherein the support comprises a layer of alumina-containing bricks.

9. Claus reaction furnace as claimed in any one of the claims 1-4, wherein the rigid permeable catalyst structure comprises a layer of particles arranged between vertical screens.

10. Claus reaction furnace as claimed in any one of the claims 1-4, wherein the rigid permeable catalyst structure comprises fibres having a thickness between 0.1 and 5 mm.

11. Claus reaction furnace substantially as described in the specification with reference to the accompanying drawing.

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